(54) Title: FUEL ADDITIVE COMPOSITION AND ITS PREPARATION

(57) Abstract: A fuel additive composition for the reduction/removal of vanadium-containing ash deposits in gas turbines and other by combustion of vanadium-containing fuel driven apparatuses, which composition as its active ingredient comprises a compound of a metal capable of forming a vanadate with vanadium of said ash deposits is disclosed.

FUEL ADDITIVE COMPOSITION AND ITS PREPARATION

Technical field

5   The present invention relates to a fuel additive composition
for the reduction/removal of vanadium-containing ash depos-
its, a process for the preparation of such a composition and
the use of certain inorganic oxygen-containing metal com-
pounds as a component of such a composition. More particu-
10   larly the present invention relates to a fuel additive compo-
sition for the reduction/removal of vanadium-containing ash
deposits in gas turbines and other by combustion of vanadium-
containing fuel driven apparatuses, a process for its prepa-
ration and the use of certain inorganic oxygen-containing
15   metal compounds as an active component thereof.

Background art

Fuels such as unrefined crude oil and residual oil containing
20   large amounts of impurities, which result in corrosive depos-
its in apparatuses driven by the combustion of such fuel. One
such impurity is vanadium, which forms catastrophically, cor-
rosive low-melting slag. Said slag can destroy vital parts
within a short time. Crude oils usually contain vanadium in
25   an amount within the range of 1-500 ppm depending on the
source of the oil. Because of its origin as a concentrate
from the refining process, residual oil contains several
times more vanadium than the crude from which it is derived.
Combustion of such vanadium-containing fuels primarily re-
30   sults in the formation of vanadium pentoxide, V_2O_5, which
melts at about 675°C. In molten state V_2O_5 behaves as an ex-
cellent solvent for e.g. the metal oxides that high tempera-
ture alloys used in the hot section of gas turbines form in
order to protect their surfaces. Thus molten V_2O_5, acting as
35   a solvent, strips away said metal oxides. The metal atoms on
the surface of the gas turbine section in contact with the
combustion gases respond by forming a new layer of oxide
coating which is again stripped away by the V_2O_5 and so on.

In gas turbines metal temperatures can be higher than 1000°C at which temperatures corrosion can proceed very fast so that the hot section may be destroyed within a week if no measures are taken to inhibit the corrosion cycle.

In order to overcome the corrosion problems caused by V_2O_5 the so-called oil soluble magnesium products were developed. These products are based on the ability of magnesium compounds to react with V_2O_5 to form a vanadate. Early products belonging to this group contained magnesium naphthenates which in the next step of development were replaced by compositions based on magnesium sulfonates. The third generation of oil soluble magnesium products comprises magnesium carboxylate products.

Thus, for instance, US RE 32653 discloses a method for the preparation of a magnesium-containing complex by heating, at a temperature above about 30°C a mixture consisting essentially of

(A) at least one of magnesium hydroxide, magnesium oxide, hydrated magnesium oxide or a magnesium alkoxide;

(B) at least one oleophilic organic reagent consisting essentially of an aliphatic cycloaliphatic or aromatic carboxylic acid containing at least eight carbon atoms or an ester or alkali metal or alkaline earth metal salt thereof;

(C) water; and

(D) at least one organic solubilizing agent for component B.

The oil soluble magnesium products are added to the fuel in an amount sufficient to convert V_2O_5 to magnesium orthovanadate, $Mg_3V_2O_8$, which melts at above 1100°C. Said temperature is below the typical gas turbine temperature when introducing the additive composition in the combustion chamber, but above the turbine gas inlet typical temperature due to the flame cooling process. Thus there will be no liquid V_2O_5 that will act as a solvent for the alloy surface metal oxides and thus corrosion caused by V_2O_5 is inhibited.

The first generation of oil soluble magnesium products had a
concentration of magnesium as low as about 4%. The concentra-
tion was increased in the second generation up to about 14%
magnesium and in the third generation the concentration could
be raised further. However, there is a continued need for
fuel additive compositions with still higher concentrations
of magnesium or other metals capable of forming vanadates
having a melting point above that of vanadium pentoxide.

Moreover, these prior art compositions give a dense vanadate
deposit the removal of which may cause some trouble.

As an alternative to oil soluble magnesium products US-A-4
412 844, issued November 1, 1983, suggests oil dispersible
aqueous dispersions of magnesium hydroxide comprising in per-
centages by weight:

(a)   20-70% magnesium hydroxide having particle size from
       1.0-50 microns;

(b)   29-79% water;

(c)   1.0-8.0% of a water-dispersible, oil-soluble, water-in-
       oil emulsifying agent having an HLB value of from 4-10;

(d)   0.1-6% of a water-soluble, oil-dispersible emulsifying
       agent having an HLB of from 20-40.

Such slurries do not allow chemical high efficiency inhibi-
tion for ash melts due to the large crystal size. This patent
states the preferred particle size to be in the range of
about 30-2 microns, which makes the composition only practi-
cally applicable per se to boilers. Thus it is expressly
stated that the magnesium hydroxide slurry specifically dis-
closed in the working example "would be utilized to control
vanadium corrosion in a utility boiler".

In addition such slurries have a limited stability.

Accordingly, it is an object of the present invention to pro-
vide a fuel additive composition containing a high concentra-
tion of magnesium or other metal capable of forming vanadates
having a melting point above that of vanadium pentoxide.

It is another object of the present invention to provide a
fuel additive composition, which on use gives a porous va-
nadate deposit that is easily removed.

It is a further object of the present invention to provide a
fuel additive composition, which is stable for a long time
such as 12 months and longer at ambient temperature.

These and other objects are achieved by means of the fuel ad-
ditive composition and the process for its preparation ac-
cording to the present invention.

Summary of the invention

The present invention is based on the discovery that crystal-
line particles of inorganic oxygen-containing metal compounds
which when suddenly being subjected to high temperatures al-
most "explosively" liberate a gaseous substance by evapora-
tion, such as water vapour or carbon dioxide in case of e.g.
magnesium hydroxide and magnesium carbonate, respectively,
and are converted to particles of the corresponding metal ox-
ide having a structure of increased porosity and reduced den-
sity when compared to a corresponding oxide prepared by
evaporation of gas at considerably lower temperatures. This
makes the oxide better suited for reaction with vanadium pen-
toxide will percolate easier into the more porous particles.
The presence or formation of such more porous particles ad-
mits a faster chemical reaction due to the fact that the ions
of V_2O_5 can travel much faster from the surface of the porous
particles along the pores surface of the lattice of said par-

ticles as vanadate forms than in the denser lattice of non or
low porous crystalline oxide.

It was also surprisingly found that when using an inorganic
oxygen-containing metal compound, which liberates a gaseous
substance by evaporating when being suddenly subjected to the
heat of a combustion flame, or a porous low density oxide
with a particle size distribution essentially within the
range of from 0.1 to 2 micron as the active ingredient of a
fuel additive composition the vanadate deposit formed was
much easier to remove than the vanadate deposit formed when
using prior art compositions.

The said particle diameter less than 1-2 μm as a measurement
of particle size is just a rough indicative measurement, as
total mass, density, shape and porosity are important "size"
properties to be considered as optimizing a fuel additive
dispersion and its functional properties on ash melts and
corrosion inhibition as well as deposit problems concerned.
The optimal "size" in all the size dimensions named will
minimize deposit buildups due to the particles kinetic ad-
sorption/desorption rate, preferably approaching 1,0 and
thereby avoiding high adsorbing atomized and <~100 nm and
avoiding high impaction rate into deposit by dense particles
above the upper, >-1000 nm, micron sized limit.

Moreover, it was found that by proper selection of the dis-
persing system, for an oil soluble solvent system, avoiding
water to the largest extent possible and using a specific
process for the preparation of the fuel additive composition,
it was possible to increase the level of the concentration
per volume unit of the metal to a level not having been dis-
closed previously for submicron and nano-sized additives.
Thus, according to the invention a combination of at least
one liquid selected from the group consisting of liquids
soluble in oil on one hand and at least one dispersant se-
lected from the group consisting of low molecular weight dis-

persants and high molecular weight dispersants on the other
is used as the dispersing system.

Thus, in accordance with a first aspect of the present inven-
tion there is provided a fuel additive composition for the
reduction/removal of vanadium-containing ash deposits in gas
turbines and other by combustion of vanadium-containing fuel
driven apparatuses, which composition as its active ingredi-
ent comprises a compound of a metal capable of forming a va-
nadate with vanadium of said ash deposits, which composition
comprises

a) as said compound of a metal capable of forming a
     vanadate with vanadium of said ash deposits a1) an
     inorganic oxygen-containing compound of said metal
     in particle form, which oxygen-containing compound,
     when heated up in a combustion flame, liberates a
     gaseous substance by evaporation and forms the cor-
     responding metal oxide having a crystalline porous
     low density structure, or a2) said corresponding
     metal oxide having a crystalline porous low density
     structure, said inorganic oxygen-containing com-
     pound a1) and said corresponding metal oxide a2)
     having a particle size distribution essentially
     within the range of from 0.1 to 2 micron, prefera-
     bly from 0.1 to 1 micron and said corresponding
     metal oxide a2) having a density of at most 2.0
     g/cm^3,

     dispersed in
b) at least one liquid selected from the group con-
     sisting of liquids soluble in oil,

     by means of
c) at least one dispersant selected from the group
     consisting of low molecular weight dispersants and
     high molecular weight dispersants.

According to another aspect of the present invention there is
provided a process for the preparation of a fuel additive
composition according to the invention, which process com-
prises

mixing a powder of an inorganic oxygen-containing compound of
a metal capable of forming a vanadate with vanadium of ash
deposits from vanadium-containing fuel and which inorganic
oxygen-containing compound when heated up in a combustion
flame liberates a gaseous substance by evaporation to form
the corresponding oxide having a crystalline, porous low den-
sity structure or a powder of said oxide having a crystal-
line porous low density structure into a mixture of at least
one liquid selected from the group consisting of liquids
soluble in oil with at least one dispersant for said inor-
ganic oxygen-containing compound or oxide selected from the
group consisting of low molecular weight dispersants and high
molecular weight dispersants using shear forces to form a ho-
mogenous pumpable premix and

subjecting the premix to a treatment comprising size degrada-
tion and dispersant coating to a particle size distribution
of the inorganic oxygen-containing metal compound and oxide
essentially within the range of from 0.1 to 2 micron, pref-
erably from 0.1 to 1 micron, under centrifugal or oscillation
forces in the presence of a grinding medium and/or ultrasonic
treatment until a plot of the sediment height in samples
taken periodically during said treatment and centrifuged at a
fixed rate for a fixed period versus time plateaus and the
viscosity has decreased and come into a steady state.

In accordance with a further aspect of the present invention
there is provided the use of an inorganic oxygen-containing
compound of a metal selected from the group consisting of
metals capable of forming vanadates having a melting point
within the range of from 650°C to 2000°C with vanadium of ash
deposits from vanadium-containing fuel, which inorganic oxy-
gen-containing compound when heated up in a combustion flame

liberates a gaseous substance by evaporation to form the cor-
responding oxide having a crystalline, porous low density
structure, or the corresponding oxide obtained by heating the
inorganic oxygen-containing compound at a temperature which
5   is high enough to give the oxide in crystalline porous low
density state but is below the melting point of the oxide,
said inorganic oxygen-containing compound and said crystal-
line porous low density oxide having a particle size distri-
bution essentially within the range of from 0.1 to 2 micron,
10 preferably from 0.1 to 1 micron, as a component of fuel addi-
tive compositions for the reduction/removal of vanadium-
containing ash deposits.

Detailed description of the invention

15

Vanadium-containing fuels are used within several fields of
apparatuses driven by the combustion of fuel. The corrosion
problems caused by the presence of vanadium may be most seri-
ous in the case of gas turbines but such problems also exist
20 in connection with e.g. boilers and diesel engines, wherein
the metal temperatures are lower than in gas turbines and
relatively less hazardous but still serious corrosion prob-
lems compared to gas turbines exist.

25 According to the present invention the metal of the inorganic
oxygen-containing compound or oxide to be used in the inven-
tion should be chosen so that on reaction with the vanadium
pentoxide a vanadate is formed that has a melting point ex-
ceeding the temperature at which the composition is used.
30 Thus, in case of gas turbines a metal should be chosen the
melting point of the vanadate thereof preferably exceeds
1100°C. Examples of such metals are magnesium the vanadate of
which melts above 1100°C and yttrium the vanadate of which
has a melting point above 1800°C, magnesium being the pre-
35 ferred metal of these two metals for economical reasons. Ex-
amples of other vanadates having melting points enabling
their use in the compositions according to the invention to
be used in connection with apparatuses of lower temperature

are among others, solely or in combinations, aluminum, zirconium, manganese, iron, copper, nickel and calcium. Often other metals than e.g. magnesium are either both rear and expensive or are environmental polluters, e.g. manganese etc.

Depending on the specific field of use generally metals capable of forming vanadates having a melting point within the range of from 650°C to 2000°C.

Due to contaminants present in the fuel the vanadates formed may be contaminated therewith resulting in a decrease or an increase of the melting point in comparison with 100% pure vanadate. Consideration should be paid thereto when selecting the metal compound or oxide used in the composition according to the present invention.

In accordance with one embodiment of the fuel additive composition according to the present invention the active ingredient thereof comprising an inorganic oxygen-containing compound of a metal capable of forming a vanadate with vanadium of ash deposits is a hydroxide of said metal which hydroxide when heated up in a combustion flame is converted to the corresponding oxide having a crystalline porous low density structure.

As indicated previously, hydroxides such as, for instance, magnesium hydroxide, may be dehydrated almost "explosively" at very high temperatures (over 1000°C and below 2800°C) to form the corresponding metal oxide. Unlike the oxides formed by dehydration of hydroxides at lower temperatures (such as just above the dehydration point of 350°C for the conversion of magnesium hydroxide to magnesium oxide) resulting in oxides with a more dense crystalline structure the oxides formed at the higher temperatures [below the upper limit in the "dead burned" range where the oxide density closely approaches the maximum density] are more porous and have a less dense crystalline structure than else.

According to another embodiment of the fuel additive composi-
tion according to the present invention said inorganic oxy-
gen-containing compound of a metal capable of forming a va-
nadate with vanadium of ash deposits is a metal carbonate.
When suddenly being heated at high temperatures such as in a
combustion flame the carbonate will liberate carbon dioxide
and form the corresponding metal oxide having a crystalline
porous low density structure analogously to the formation of
the oxide from an hydroxide at very high temperatures.

According to a further embodiment of the fuel additive compo-
sition according to the present invention said compound of a
metal capable of forming a vanadate with vanadium of ash de-
posits is a metal oxide having a crystalline porous low den-
sity structure. Such oxides may, for instance, be prepared
from the corresponding hydroxides or carbonates by heating at
a high temperature. In order to obtain maximum porosity of
the oxide the conversion of the hydroxide or carbonate should
be carried out below the point at which the oxide tends to
increase in density, but close thereto and far below it
starts melting. Above said point at which the oxide "tends to
start melting" the pore structure continually decreases as
approaching the critical melting point, at which maximum den-
sity will be reached, for e.g. magnesium oxide at 2750°C.
Such a heat treatment to achieve minimum porous density oxide
may be performed by passing a dry powder of an optimal size
distribution of the hydroxide or carbonate through a flame
having a temperature suitably adapted below the density de-
creasing point of the oxide as indicated above.

Alternatively, low density metal oxides may also be prepared
by suddenly subjecting submicron sized crystals of an inor-
ganic oxygen-containing metal compound, preferably a hydrox-
ide or a carbonate, which when heated to a high temperature
liberates a gaseous substance by evaporation, to heating at
an appropriately high temperature in an oven. Thus, for in-
stance, the present inventors rapidly heated sub-micron sized
particles of magnesium hydroxide in an oven at a temperature

of 1000°C for a short time which resulted in the conversion
of the magnesium hydroxide into magnesium oxide having a den-
sity of ~ 1.4 g/cm^3. Similar heating of magnesium carbonate
in an oven at a temperature of 1300°C resulted in magnesium
5   oxide having a density as low as 1.03 g/cm^3

According to the present invention the low density metal ox-
ide should preferably have a density of at most 2.0 g/cm^3,
more preferably below 1.5 g/cm^3 and most preferably below 1.0
10   g/cm^3.

The inorganic oxygen-containing metal compounds and porous
low density metal oxides incorporated in the fuel additive
composition according to the invention should have a particle
15   size distribution essentially within the range of from 0.1 to
2 micron, preferably from 0.1 to 1 micron, preferably nar-
rowly distributed close to the optimal size within that range
of 0.1 to 1 micron. Preferably said compounds and oxides
should have a particle size optimal distribution which is
20   adapted to be most effective at the temperature at which a
solid, porous metal vanadate is formed and to form ash parti-
cles which deposit as little as possible [due to thermody-
namic surface adsorption and desorption properties of the
particles] and form as loose a deposit as possible [due to
25   the porosity of the particles and thereby the epitactic and
topotactic deposits lattice build-up structure].

According to the high initial flame maximum temperature in
the range of 1600-2000°C before cooling the gas the particle
30   size distribution should be selected so that the metal va-
nadates formed in the flame are not given sufficient time to
melt before reaching areas of the apparatus having a tempera-
ture below the melting point of the vanadates. Moreover, the
porous oxides added to the fuel are not delayed in their re-
35   action to the formation of the vanadates in the heat zone
compared to the porous oxides formed from, for instance hy-
droxides or carbonates bypassing the heat zone. This means
that in case of gas turbines in which the temperature of the

flame may be as high as around 2000°C, a hydroxide or a car-
bonate should be used which has a particle size which is
greater than that of the same hydroxide or carbonate to be
used in apparatuses operating at a lower heat zone flame tem-
5   perature. Furthermore, due to their higher reactivity surface
enlarged porous metal oxides should be used at temperatures
lower than those prevailing in gas turbine heat zones, i.e.
they may preferably be used in boilers and diesel engines if
an extraordinarily low operating temperature in the heat zone
10 would be a disadvantage of the addition of the heat zone by
passing metal hydroxide into the fuel.
Moreover, it was found that conversion of magnesium carbonate
into magnesium oxide at a given temperature is a slower proc-
ess than the conversion of magnesium hydroxide to the oxide
15 due to the difference in energy required to evaporate the
carbon dioxide from the carbonate in comparison with water
from the hydroxide. This means that in apparatuses working at
relatively low temperatures (e.g. boiler and diesel engines)
the use of magnesium hydroxide particles may be the preferred
20 choice whereas magnesium carbonate might be preferred for use
in connection with gas turbines having an extremely high tem-
perature in the flame in order to obtain a low density of the
oxide formed.

25 Of specific importance is that the size of the oxide parti-
cles is in the range not below 0.1 micron and not above high
density impacting 2 micron, preferably exhibiting a particle
size distribution injected into the fuel around 0.4 to 0.5
micron, in order to reduce the deposit accumulation due to
30 the Brown Movement Kinetic affecting the particles surface
adsorption and desorption rate on the deposit surface and
that the said particles have a surface area including inter-
nal pores surface interface area comparable to that of crys-
talline high density oxide particles of a particle size far
35 below 0.1 μm to maximize the reactive surface. Such a high
surface area will solely be achievable by porous particles.

The inventors have noted that dehydration or evaporation of magnesium hydroxide particles at high temperature causes a split size reduction and volume expansion and agglomeration into a less tight particle size distribution depending on the

5   particles individual initial size. For this reason the particle size of the particles used in the fuel additive compositions according to the invention will generally be distributed in a somewhat enlarged size range below and above when using the hydroxide in comparison with the use of a size tai-

10 lored oxide.

The particles of the inorganic oxygen-containing compound as well as the oxide particles should preferably have a narrow (low variance) particle size distribution, preferably around

15 a cross section largest distance arithmetic mean in the 0.2 to 0.5 micron range and with a variance for a lognormal distribution in the range ~0.2 < δ < ~0,6.

In the fuel additive composition according to the present in-

20 vention the inorganic oxygen-containing metal compound or oxide particles are dispersed in at least one liquid selected from the group consisting of liquids soluble in oil.

Contemplated for use in the fuel additive composition accord-

25 ing to the invention are liquids selected from the group consisting of mineral oils, synthetic oils, highly aromatic naphtha, diesel oil, vegetable oils, esterified vegetable oils, animal oils and esterified animal oils.

30 Examples of vegetable oils and esters thereof to be used in the fuel additive compositions according to the invention include, but are not limited to, peanut oil, coconut oil, corn oil, linseed oil, rape-oil, palm oil, sunflower oil, olive oil, tall oil and esters thereof, the preferred representa-

35 tive thereof being rape-oil methyl ester (RME).

Examples of animal oils to be used in the fuel additive compositions according to the invention include, but are not

limited to, fish liver oil, train-oil and liquid modified fat
from slaughter-houses.

The preferred representatives of the liquids soluble in oil
to be used in the present invention are diesel oil and rape-
oil methyl ester.

According to the present invention the inorganic oxygen-
containing metal compound particles or metal oxide particles
have become dispersed in at least one liquid which, as stated
above, is selected from the group consisting of liquids solu-
ble in oil by means of at least one dispersant selected from
the group consisting of low molecular weight dispersants and
high molecular weight dispersants.

The term "low molecular weight dispersants" as used here and
in the claims is used to designate dispersants having a mo-
lecular weight usually within the range of from 1.000 to
2.000g/mole. In addition, dispersants may be classified to
manifold properties as described below.

The term "high molecular weight dispersants" as used here and
in the claims is used to designate dispersants having a mo-
lecular weight usually within the range of from 5,000 to
30.000 g/mole.

In addition. the conventional low molecular weight dispers-
ants are categorized according to their structure as anionic,
cationic, amphoteric and nonionic. Their efficiency is de-
fined by a) absorption of polar groups to the surface of the
particles to be dispersed and b) the behavior of a non-polar
chain of the medium surrounding the particle.

The dispersant industry supplies a huge variety of efficient
steric dispersants that enables stable solid particle disper-
sions for colloid oil and aqueous systems. A colloid is a
liquid droplet or a solid particle in the size range of at
most 1-2 μm but normally submicron or in the range of one

molecule to many molecules forming a size of 2 -999 nm in av-
erage diameter. Steric dispersants adsorb and coat the parti-
cle surfaces. A surface is an interface between two non-
soluable compounds, one liquid and one solid state or two
liquid states. As no interface or surface occurs between the
dispersant-particles-layer-tails penetrating into the parti-
cles ambient solvent the colloid dispersion is a true disper-
sion formed of particles and such dispersions is commonly de-
fined as a micelle dispersion. A huge group of steric dis-
persants forms micelles both in oil and water systems.

Most steric dispersants form micelles in a selected oil solu-
ble solvent, when the hydrophobic tail penetrates into the
solvent. The stability of such dispersions is depending on
many different forces defining the stability boundaries for
the other unit tail. The other said molecular hydrophilic
tail adsorbs to the particle surface and will be bondable to
the surface of the particle in many different ways due to the
kind of (1) anchor groups, (2) the number of repeating units
in the polymer and (3) if the dispersant is a homo polymers
dispersants whereas the repeating units are of one kind or is
a co-polymer of two different kinds and (4) the electrostatic
properties.

The known art of the described colloid dispersion systems ad-
mits a suitable tool to tailor a stable composition of solid
particles suitable as a fuel additive. In the range of suit-
able compounds magnesium carboxylates and magnesium sul-
fonates has been widely used to create stable metal oxide
dispersions in fuel additives. In the disclosed invention
the kind of dispersants suitable is enlarged to admit higher
concentrations of stable solid dispersions. Among others we
have tested Hypermer® LP4 (amine derivate of a fatty acid
condensation polymer, from UNIQEMA, Everberg, Belgium) EFKA
4010 (modified polyurethane, from EFKA Inc., Heerenveen, the
Netherlands) and Rhodafac® RE 610 (nonylphenol ethoxylate
based phosphate esters, from Rhodia Inc, France). All of
these dispersants among others fulfill the claim to form sta-

ble dispersions of magnesium oxides and magnesium hydroxides
and other particles if a suitable solvent and dispersion
technology is applied.

5   The selection of a dispersant for a specific application has
to be done due to the different claims of stability due to
ambient boundaries i.e., solid concentrations, temperature,
g-forces and the desired viscosity for the composition. To
achieve maximum particle concentration the dispersant layer
10   that coats the particles has to be thin. This is achieved by
a small low molecular weight dispersant as characterized by
Rhodafac® RE 610 having two tail units penetrating into the
solvent or Hypermer® LP4. When the volume of solvent in the
composition increases and the particle concentration is lower
15   it is suitable instead to choose a high molecular weight dis-
persant for instance EFKA 4010. When low particle concentra-
tions are desired other dispersants may be preferably ap-
plied, but for such applications the particle size range is
of basic importance due to solvent molecules Brown Movement
20   Kinetics. In addition simple non-steric solely and electro-
static dispersants, such as low molecular waxy compound e.g.
modified or non modified lanoline extracts from sheep wool
fat-layer may be applied.

25   High molecular weight dispersants have pendent anchoring
groups, which adsorb to the surface of the particles to be
dispersed. Their mechanism of action is by hydrogen bonding,
dipole-dipole interactions or Van der Waal forces. The poly-
meric framework is sufficiently great to give an effect
30   called sterical stabilization.

The preferred dispersants to be used in the present invention
are anionic and amphoteric low molecular weight dispersants.

35   Although, anionic low molecular weight dispersants to be used
in the present invention include magnesium soaps of carbox-
ylic and sulfonic acids. Such dispersants and comparable dis-
persants containing magnesium are not preferable, as they may

comprise atom sizes magnesium that depart from the scope of porous oxides feature, as a partial or total disadvantage to the aimed invention.

5   The fuel additive composition according to the present invention will generally comprise the submicron or nano-sized inorganic oxygen-containing metal compound or oxide (component a)) in a concentration of from 10 to 65% by volume, preferably from 20 to 50% by volume and more preferably from 30 to
10   50% by volume, and most preferably from 40 to 50% by volume, calculated on the total volume of the compositions, the balance to 100% by volume essentially consisting of components b) and c) and possibly a minor amount of water (generally less than 0.5% by volume) such as moisture emanating e.g.
15   from the use of not fully dry starting materials, such as the hygroscopic substance magnesium hydroxide or deliberately added to regulate the viscosity and stability of the composition.

20   The upper limit of the concentration of inorganic oxygen-containing compound or oxide in each specific case is defined by the particle volume size and specific dispersants depletion limit due to the specific particle size that may destabilize the dispersion. Thus the upper limit will increase
25   with increasing average particle size. Thus, for instance, the upper limit will be around 50% by volume in case of particles having a particle size low variance distribution, as a distribution having variance from ~0.2 to ~0.6 for the log-normal distribution around a mean size from 500 to 200 nano-
30   meters (nm) respectively

The volume ratio component b) to component c) generally depends on the specific substances used as those components and the amount of particles to be dispersed. The optimum ratio in
35   each specific system may easily be determined in a series of experiments varying said ratio for which experiments no inventive activity should be required.

-18-

The fuel additive composition according to the invention is
prepared according to said another aspect of the invention by
means of the process according to the invention, which proc-
ess comprises

5

mixing a powder of an inorganic oxygen-containing compound of
a metal capable of forming a vanadate with vanadium of ash
deposits from vanadium-containing fuel and which inorganic
oxygen-containing compound when heated up in a combustion
10   flame liberates a gaseous substance by evaporation to form
the corresponding oxide having a crystalline, porous low den-
sity structure or a powder of said oxide having a crystal-
line porous low density structure into a mixture of at least
one liquid selected from the group consisting of liquids
15   soluble in oil with at least one dispersant for said inor-
ganic oxygen-containing compound or oxide selected from the
group consisting of low molecular weight dispersants and high
molecular weight dispersants using shear forces to form a ho-
mogenous pumpable premix and

20

subjecting the premix to a treatment comprising size degrada-
tion and dispersant coating to a particle size distribution
of the inorganic oxygen-containing metal compound and oxide
essentially within the range of from 0.1 to 2 micron, pref-
25   erably from 0.1 to 1 micron, under centrifugal or oscillation
forces in the presence of a grinding medium and/or ultrasonic
treatment until a plot of the sediment height in samples
taken periodically during said treatment and centrifuged at a
fixed rate for a fixed period versus time plateaus and the
30   viscosity has decreased and come into a steady state.

Metal compound particles to be used in the process according
to the present invention should not contain crystal water and
have a low moisture content, if necessary obtained by a dry-
35   ing process, preferably a moisture content far below 0.5% by
weight.

The particle size of the metal compound or oxide particles
should not be exceedingly greater than the size of the parti-
cles of composition prepared by means of the process and gen-
erally particle sizes within the submicron range should be
5   used, but small particles of a substantial amount below 0,1
microns easily adsorbing the deposit areas and having a low
desorbtions rate should be avoided.

According to a preferred embodiment of the process according
10 to the present invention the particles of the metal compound
or oxide are added to a vessel containing a mixture of said
at least one liquid selected from the group consisting of
liquids soluble in oil and at least part of said at least one
dispersant under mixing to form a premix allowing the tem-
15 perature to rise during the mixing, e.g. to a temperature
within the range of from 50°C to the upper limit ~85°C de-
fined by the centrifugal forces and the viscosity to avoid
cavitation of the grinding media in order to reduce the vis-
cosity of the premix.
20
For the procedure of the second step of the process according
to the present invention preferably a basket mill is used.
Such mills are available on the market and are, for instance,
sold in different models under the trade name Turbomill by
25 Mirodur SpA, Aprilia, Italy.

The grinding media used are e.g. small zirconium balls, the
diameter of which is chosen in accordance with the intended
particle size of the metal compound and oxide particles, re-
30 spectively, after grinding so that said diameter is increased
when larger particles are wanted. Generally said diameter
will be within the range of from 0.8 to 1.2 mm, however,
balls of uniform size being used in each specific case. Balls
of other materials known as suited for use as grinding media,
35 e.g. steel and glass, can also be used in the process accord-
ing to the invention.

A zirconium ball size of 0.8 mm is, for instance, sufficient
to reach the desired size for e.g. $Mg(OH)_2$-particles and ef-
ficiently disperse the particles in accordance with the in-
vention.

The premix mentioned above is filled into the basket mill
vessel and rotating is started and speeded up to full power
loading allowing temperature to rise to about 75-85°C. All
moisture that evaporates during the basket mill operation
should be evacuated from the vessel.

Samples are taken at intervals of 30 to 70 minutes such as 1
hour and centrifuged at a fixed rate, e.g. within the range
of from 2000 rpm to 4000 rpm, such as 3000 rpm, for a fixed
period within a range of from e.g. 30 minutes to 1 hour, such
as 45 or 50 minutes, and the height of the sediment of each
sample measured. During rotation of the basket the height of
the sediment of the different centrifuged samples will start
to decrease rapidly as sampling proceeds. Rotation is contin-
ued during a constant temperature operation phase until the
plot of sediment height versus time plateaus and thereby the
basic viscosity has decreased and come into a steady state.

As an alternative to the rotating basket mill operation
grinding may be performed by means of oscillation buckets.
Alternatively or as a supplement to grinding ultrasonic
treatment may be applied.

The design of grinding mills commonly supplied has to be ad-
justed for the engine effect upwards to achieve at least an
accelerative force above 50 g on the liquid to reach the
limit force needed to override the tensions to disaggregate
the present smallest nano particles. Preferably 70 g is
needed as desired to economically optimize the capacity dis-
persed per kWh etc.

The liquid lubricant film must hold the balls of e.g. a bas-
ket mill apart from each other. Otherwise the cavitating

balls will degrade themselves rapidly. There is no possibil-
ity to achieve static pressure to degrade agglomerates and
grind nano-scaled particles. The force here transmitted, to
achieve degradation has to be transmitted to the electromag-
netic interference between particle surfaces and the interme-
diate liquid.

A media mill optimizing the following parameters preferably
achieves this.

1. Temperature
2. Relative content of solids in the liquid
3. Ball size
4. Ball density
5. Ball volume relative to inlet power to be transmitted.
6. Accelerative force in g-number (Af)

Media disc mills are not suitable as accelerative force
achievable is to low.

Commonly in the color industry applied basket mills e.g. a
Turbomill is suitable for the present purpose. But other
kinds of mills as e.g. high frequency oscillation ball media
vessels as e.g. the Colorox mill may be applied. By rotating
the ball filled basket in a Turbomill the acceleration force
(a) will be distinctly controlled by the rotation speed.

Equation (1) $a = (\omega^2 * r*2*\pi)$; m/s^2

Where: r = peripheral radius in meter for the basket
                    or a body orbit

                ω = angular velocity = rpm/60 = cycles per
                    second = Hertz

        and   1 Newton = 1 m/ s^2;   and Af = a/9.82; g

As recognized by equation (1) the acceleration force is pro-
portional to the radius for a body motion in a circular orbit
and proportional to the square power for the angular veloc-
ity. Thereby, the needed rpm or frequency for different or-

bits to reach the acceleration to override the tension is
given by:

Equation (2)   ω = Square root of (Af*9.82*/r)   divided   by
(2*π*60)

An acceleration force (Af) of 70g is preferable to exceed the
tensions in the crystal aggregate. Thereby equation (2) tells
us the orbit frequency for different kind of mills and other
kinds of power transmission facilities. As we decrease the
orbit radius to a certain limit e.g. 10 mm we cannot apply
the power by centripetal force as in a basket mill of under-
standable reasons. Instead an high frequency oscillatory or
vibrato vessel is preferable. A 210 mm radius basket needs a
rotating speed of 546 rpm to achieve a peripheral force of
70g. A small body in 10 mm radius oscillatory vessel needs a
rotation speed of 3541 rpm or 59 Hertz.

To roughly define the velocity property limit to be override
for different kinds of force transmission equipment in accor-
dance with the invented process to prepare the dispersion for
the invented composition we need the illustrative tube. Imag-
ine a tube that enables to apply accelerative force in in-
versed direction for the liquid in one direction and the tube
wall in the other direction. Thereby the relative speed and
the tension between the liquid and the tube wall will define
the sheer forces interfering the particles. As the entire
volume in an oscillatory vessel will oscillate in small or-
bits the relative speed will reach approximately a maximum of
twice the peripheral oscillation speed. Thereby the shear
force limit will be reach at a frequency of 2504 rpm or 42
Hertz for a 10 mm radius oscillatory vessel instead of said
frequency of 59 Hertz above for a single small body accelera-
tion of 70g.

In addition ultrasonic methods may be used, as dispersion par
se is desired. Similar to the oscillatory vessel case equa-
tion (2) will help us to define the frequency for different

ultrasonic amplitudes or wavelengths to be applied. As a con-
ventional ultrasonic frequency is 20-40 kHz for e.g. 35 kHz
the desired amplitude is 15 nm, but a substantially higher
amplitude in the range above 1-10 microns is a necessity due
to achieve sheer beams for the entire particles and not only
for a small limit part on a particles surface area. The am-
plitude has to substantially exceed the particles size to ad-
mit surface coating and particles to cavitate. Thereby, ul-
trasonic equipment is also contemplated for use in the pre-
sent invention, especially as increased power density is
needed to achieve efficient fast coating on the small part of
the very small nano particles to get a fully stable disper-
sion not reaggregating.

The invention will now become illustrated by means of a num-
ber of non-limiting working examples illustrating the prepa-
ration and use of the compositions according to the inven-
tion.

Examples
Materials used in Examples 1 & 2

The magnesium hydroxide used was Ankermag®-HH from Magnifin
Magnesiaprodukte GmbH, Austria. The magnesium powder contains
> 98.0 % by weight (wt%) $Mg(OH)_2$ and < 0.5 wt% water. Spe-
cific surface 9-12 m^2/g equivalence a mean size for a dense
sphere diameter range from 200-260nm or in fact the largest
diameter of the thin flakes crystals average ~500nm. The
crystals D50 diameter is ~900 nm, i.e. the median size diame-
ters in the distribution. In addition the crystal agglomerate
upper limit diameter is less than approximately 50 microns.
The preparation process according to the invention admits
feeding by much larger particles, preferably a surface area
above > 3-4 m^2/g.

The dispersant used was Rhodafac® RE 610, from Rhodia Inc, France, which is characterized by the manufacturer as nonyl-phenol ethoxylate based phosphate esters.

5   Rape-oil methyl ester was supplied by Svenska Ekobränslen AB, Sweden.

Example 1: Preparation of fuel additive composition-batch of 1000 kg

10

20 kg of Rhodafac® RE610 and 270 kg of rape-oil methyl ester (RME) having a moisture content of <0.05% by weight were mixed in a dissolver vessel (Disolver DTM49 from Westerlins Maskinfabrik AB, Malmö, Sweden) to a homogenous mixture.

15

Then 690 kg of magnesium hydroxide powder dried to a moisture content of <0.5% by weight were gradually added under continued mixing allowing the temperature to rise to about 50°C to form a premix.

20

The premix was then transferred to the vessel of a basket mill (Turbomill® 2, from Mirodur SpA, Aprilia, Italy, with an engine effect of 55kW) containing balls of zirconium having a diameter of 0.8 mm as the grinding medium and rotation of the
25 basket was started and speeded up to full power loading.

The temperature was allowed to increase to 75°C-85°C, i.e. securely below the upper limit where the reduced viscosity achieved by the increase in temperature will allow the balls
30 of the milling medium to touch each other by chance.

The temperature was kept stable until the samples taken at intervals of 1 hour and centrifuged at a rate of 3000 rpm for 50 minutes indicated a rapid decrease in the height of the
35 pellet obtained by such centrifugation after approximately 4-6 hours, due to operation temperature and the applied centrifugal force. The basket mill was kept running until the

premix was fully dispersed which occurred as decreasing the
rotation in accordance to the decrease in the height of the
pellet obtained by centrifuging samples as above until ap-
proaching a steady state. Then additional 20 kg of Rhodafac®

5   RE610 and 20 kg of rape-oil methyl ester (in addition, if de-
sired 1-5 liter water may be added per ton to achieve in-
creased stabilization of the particles) were added and the
grinding process continued for approximately 15 minutes.

10 The completed process was shut down and the composition liq-
uid was pumped into barrels and samples were collected. If
desired for the specific applications the liquid composition
is diluted by RME before barreling it up.

15 The Mg content by ash test was ~29% by weight and the $Mg(OH)_2$
content was 69% by weight (~46% by volume) and the upper tail
of the size distribution was below 1,0 micron and the main
particle flakes shown by a standard scanning electronmicro-
scope were in the range 0.2-0.5 micron.

20

Example 2. **Preparation of fuel additive composition-batch of**
1000 kg

40 kg of a Rhodafac® RE610 and 270 kg of diesel (class 1)

25 were mixed in a dissolver vessel (Disolver DTM49 from Wester-
lins Maskinfabrik AB, Malmö, Sweden) to a homogenous mixture

Then 690 kg of magnesium hydroxide powder dried to a moisture
content of <0.5 % by weight were gradually added under con-

30 tinued mixing allowing the temperature to rise to about 50°C
to form a premix

The premix was then transferred to the vessel of a basket
mill (Turbomill® 2, from Mirodur SpA, Aprilia, Italy, with an

35 engine effect of 55kW) containing balls of zirconium having a
diameter of 0.8 mm as the grinding medium and rotation of the
basket was started and speeded up to full power loading.

The temperature was allowed to increase to 75°C-85°C, i.e. securely below the upper limit where the reduced viscosity achieved by the increase in temperature will allow the balls of the milling medium to touch each other by chance.

The temperature was kept stable until the samples taken at intervals of 1 hour and centrifuged at a rate of 3000 rpm for 50 minutes indicated a rapid decrease in the height of the pellet obtained by such centrifugation after approximately 4-6 hours, due to operation temperature and the applied g-force. The basket mill was kept running until the premix was fully dispersed which occurred as decreasing the rotation in accordance to the decrease in the height of the pellet obtained by centrifuging samples as above until approaching a steady state. Then additional 40 kg of Rhodafac® RE610 (in addition, if desired 1-5 liter water may be added per ton to achieve increased stabilization of the particles) were added and the grinding process continued for approximately 15 minutes.

The completed process was shut down and the composition liquid was pumped into barrels and samples were colleted. If desired for the specific applications the liquid composition is diluted by dieseloil before barreling it up.

The Mg content by ash test was ~29% by weight and the $Mg(OH)_2$ content was 69% by weight (~46% by volume) and the size distribution of the upper tail was below 1,0 micron and the main particle flakes shown by a standard scanning electronmicroscope were in the range 0.2-0.5 micron.

Example 3. Comparison of structures of magnesium oxide

In order to compare the structure of magnesium oxide having an porous structure formed by subjecting magnesium hydroxide to a high temperature with that of magnesium oxide prepared by dehydrating magnesium hydroxide at a comparatively lower temperature the following experiment was carried out.

Three samples of magnesium hydroxide powder having a particle
size distribution of mean 400 nm, an $\delta=0.4$ for the lognormal
estimated cross-section function and a moisture content of
<0.5 % by weight and equal in weight were used. The samples
5   were rapidly heated in an oven at a temperature of 450°C
1000°C and 1300°C, respectively.

Analyses of the 1000°C treated sample showed that the surface
area increased from BET 8.66 m^2/g for the hydroxide particles
10 to BET,10.38 m^2/g for the porous oxide particles. The density
decreased from approximately 2.3 g/cm^3 for the $Mg(OH)_2$ to
1,36 g/cm^3 (measured by a pyknometer) for the converted MgO
crystals. This is below 40% of the density of nonporous MgO
of 3.58 g/cm^3 and a remarkably low density.

15

The specific surface area for $Mg(OH)_2$ and MgO was measured by
Multipoint Surface Area N^2-gas at 77° Kelvin adsorption iso-
therm and pore distribution. The pore diameter at surface had
its distinct high frequency with as micropores within the
20 range 3.5-6.5 nm for the almost fully dense $Mg(OH)_2$ and for
the converted low density MgO as mesopores within the range
of 10-60 nm with the mode-frequency just below 30 nm

It was confirmed by X-ray diffraction (Cu, K; $\alpha=1.54 Å$) that
25 MgO has a solely crystalline lattice structure whereby the
crystals are not to any degree an amorphous unordered struc-
tured crystal. Thereby the expanded and to some extent sin-
tered crystals contain open pores through the crystal surface
as well as closed pores within the crystals due to the low
30 density and the small 20% increase in specific surface area
as loosen 3/5 atoms out of the crystal volume.

The other two samples treated at 450°C and 1300°C confirm
that the MgO density is temperature sensitive as density de-
35 creases by temperature within the temperature range below the
high temperature dead burned range above approximately
1600°C. Thereby there my be a need to tailor size low density
MgO particles for certain applications as the operating com-

bustion temperature will be below the optimal temperature to
form desired low density MgO particles to reduce deposit
buildups

5   Similary, magnesium carbonate was rapidly heated in an oven
at a temperature of 1300°C and the density of the magnesium
oxide thus formed was measured by a pyknometer and found to
be 1,03 g/cm^3

10   The results of the density measurements together with density
values found in literature are summarized in the following
table.

15   **Table**

Density of magnesium oxide formed by heating magnesium hy-
droxide and magnesium carbonate at different temperatures at
ambient atmospheric pressure.

20

Temp. [°C]	Density of MgO from Mg (OH)$_2$ [g/cm^3]	Density of MgO from MgCO$_3$ [g/cm^2]	Remark
450	2.13	-	
1000	1.36	-	
1300	2.45	1.03	
2750	3.58	3.58	from litera-ture

Example 4

25   A fuel additive composition according to the present inven-
tion was used in a large-scale comparative test in a power
plant, wherein two comparable 120 MW gas turbines were ap-
plied in parallel, both being fed with the same fuel until

injecting the composition according to the invention and a prior art composition (KL 200 from Baker Petrolite, USA), one for each gas turbine with the same present common pumps into the oil flow on its final short way into the combustion chamber. The gas turbines were completely up kept at onset including new turbine blades.

The fuel additive composition according to the invention used in this experiment had a density of ~1.56 g/cm^3 and contained ~69 % by weight of magnesium hydroxide particles and thereby 29% Mg by weight having a particles size distribution around mean ~300-500 nm with a variance mean for the lognormal distribution of ~0.4 and 4% by weight of Rhodafac® RE610 from Rhodia Inc, France and 27% by weight of REM.

KL 200 is a magnesium oxide over-based magnesium carboxylate vanadium inhibitor with a density of 1.22 g/cm^3 containing 20% Mg as specified by the supplier.

Based on laboratory test figures every second hour the dose rate was maintained at the level of 2 grams of magnesium per 1 gram of vanadium inherent in the washed heavy fuel oil containing 20-30 ppm vanadium and ~2% sulfur.

Inspections were made after each wash cycle.

The wash cycle is the time range from start of operation until the gas turbine needs to be cleaned up for deposits due to technical and economical disadvantages from the accumulated deposits of ash compounds.

It was found at the inspections for the 1st wash cycle before auto wash that the deposits were easy to remove by hand in case of using the composition according to the invention but could not be removed by hand in case of using the prior art composition.

-30-

During the 1st wash cycle in this comparative large-scale test, the input-output efficiency rate adjusted by uncontrolled variables shows an increase in average MWh output per unit oil of approximately 1% in favor to the turbine injected
5   with the additive in accordance with the invention. Thereby, it was assumed that the gas turbines run in parallel with the same fuel was comparable. The 1% efficiency difference between the gas turbines was an underestimation of the true benefits of the invented composition as illustrated in the
10   next paragraph.

During the 4th and 5th wash cycles both turbines were run with the prior art fuel additive to indicate the comparability. A difference was found. Instead of the comparison after the 1st
15   wash cycle the 3rd and 6th wash cycles for the gas turbine run by the fuel additive according to the invention were compared to the 4th wash cycle run by the prior art fuel additive. It was found that the average efficiency increased in an amount of at least 2-4% by using the fuel additive composition ac-
20   cording to the present invention.

Of special interest is the effect occurred as the turbine was tripped on the day 8 and the booster effect increased the efficiency by more the 2% units.
25

The volume of the pores in the deposits was estimated before auto wash. By letting a liquid be absorbed into deposit pieces it was found that deposits in accordance with the invention were substantially more porous in the range of an ad-
30   ditional pore volume for deposit comparable locations of 30-115% and in accordance with that a decreased density in the rage up to 25% was reported. In addition the liquid absorbance speed was much faster for the deposits in accordance with the invention.
35

Of great importance is the ability of the deposits to absorb aerosol water during auto wash and booster tripping a gas turbine. Indicatively this feature is in proper advance for

deposits formed by applying the invented composition as the absorbance of H_2O from ambient 60% relative humidity air rapidly reaches a steady state of 2.9% compared to the absorbance of deposits formed by the prior art conventional composition which was more than 10 time less or 0.25% H_2O at room temperature.

Conclusions

The findings illustrated in the examples show and fully explain the better off for gas turbine input-output efficiency for the porous MgO-particles applied in accordance with the present innovation to react in the combustion chamber instead of MgO dense-structured crystals as mainly is inherent in the combustion chamber for prior art compositions. These findings may be generalized to other solid metal-oxides, from the scientific common sense in chemistry and physics. Thereby, additional metals not tested may be applied in accordance with the disclosed invention to reduce the negative efficiency impacts of hard ash deposits in oil power transformation.

As will be apparent to those skilled in the art in the light of the foregoing disclosure, many modifications, alterations and substitutions are possible in the practices of this invention without departing from the spirit or scope thereof as defined in the appended claims.

CLAIMS

1.   Fuel additive composition for the reduction/removal of
      vanadium-containing ash deposits in gas turbines and
      other by combustion of vanadium-containing fuel driven
      apparatuses, which composition as its active ingredient
      comprises a compound of a metal capable of forming a va-
      nadate with vanadium of said ash deposits, which compo-
      sition comprises

      a)   as said compound of a metal capable of forming a
            vanadate with vanadium of said ash deposits a1) an
            inorganic oxygen-containing compound of said metal
            in particle form, which oxygen-containing compound,
            when heated up in a combustion flame, liberates a
            gaseous substance by evaporation and forms the cor-
            responding metal oxide having a crystalline porous
            low density structure or a2) said corresponding
            metal oxide having a crystalline porous low density
            structure, said inorganic oxygen-containing com-
            pound a1) and said corresponding metal oxide a2)
            having a particle size distribution essentially
            within the range of from 0,1 to 2 micron, prefera-
            bly from 0,1 to 1 micron and said corresponding
            metal oxide a2) having a density of at most 2.0
            g/cm^3,

            dispersed in
      b)   at least one liquid selected from the group con-
            sisting of liquids soluble in oil,

            by means of
      c)   at least one dispersant selected from the group
            consisting of low molecular weight dispersants and
            high molecular weight dispersants.

2.   Fuel additive composition according to claim 1, wherein
      said metal is capable of forming vanadates having a

melting point within the range of from 650°C to 2000°C.

3.   Fuel additive composition according to any of claims 1 and 2, wherein said metal is magnesium or yttrium.

4.   Fuel additive composition according to any of claims 1 to 3, wherein said inorganic oxygen-containing metal compounds or oxide has a particle size distribution which is adapted to be most effective at the temperature at which a solid, porous metal vanadate is formed and to form ash particles which deposit as little as possible and form as loose deposits as possible.

5.   Fuel additive composition according to any of claims 1 to 4, wherein said liquid is selected from the group consisting of mineral oils, highly aromatic naphtha, diesel fuel, vegetable oils, esterified vegetable oils, animal oils and esterified animal oils.

6.   Fuel additive composition according to claim 5, wherein said vegetable oils and esters thereof are selected from peanut oil, coconut oil, corn oil, linseed oil, rape-oil, palm oil, sunflower oil, olive oil, tall oil and esters thereof.

7.   Fuel additive composition according to claim 5, wherein said liquid is rape-oil methyl ester or diesel fuel.

8.   Fuel additive composition according to any of claims 1 to 7, wherein said inorganic oxygen-containing metal compound or oxide comprises from 10 to 65% by volume, preferably from 20 to 50% by volume and more preferably from 30 to 40% by volume, and most preferably from 40 to 50% by volume, calculated on the total volume of the composition.

9.   Fuel additive composition according to any of claims 1 to 8, wherein said at least one dispersant is an anionic

or amphoteric low molecular weight dispersant.

10.   Process for the preparation of a fuel additive composi-
      tion as defined in any of claims 1-8, which process com-
      prises

      mixing a powder of an inorganic oxygen-containing com-
      pound of a metal capable of forming a vanadate with va-
      nadium of ash deposits from vanadium-containing fuel and
      which inorganic oxygen-containing compound when heated
      up in a combustion flame liberates a gaseous substance
      by evaporating to form to the corresponding oxide having
      a crystalline porous low density structure or a powder
      of said oxide having a crystalline porous low density
      structure into a mixture of at least one liquid selected
      from the group consisting of liquids soluble in oil with
      at least one dispersant for said inorganic oxygen-
      containing metal compound or oxide selected from the
      group consisting of low molecular weight dispersants and
      high molecular weight dispersants using shear forces to
      form a homogenous pumpable premix and

      subjecting the premix to a treatment comprising size
      degradation and dispersant coating to a particle size
      distribution of the inorganic oxygen-containing metal
      compound and oxide essentially within the range of from
      0.1 to 2 micron, preferably from 0.1 to 1 micron, under
      centrifugal or oscillation forces in the presence of a
      grinding medium and/or ultrasonic treatment until a plot
      of the sediment height in samples taken periodically
      during said treatment and centrifuged at a fixed rate
      for a fixed period versus time plateaus and the viscos-
      ity has decreased and come into a steady state.

11.   Process according to claim 10, wherein the size degrada-
      tion and dispersant coating is carried out in a basket
      mill with zirconium balls as a grinding medium.

12. Process according to claim 11, wherein size degradation and dispersant coating is carried out at an accelerative force within the range of from 50g to 70g on the liquid.

13. Process according to any of claims 11 and 12, wherein only part of said at least one liquid and/or said at least one dispersant has been used when preparing the mixture of said at least one liquid soluble in oil and said at least one dispersant, the remainder of the dispersant and liquid being added after said graph over the sediment height in samples taken periodically and being centrifuged at a fixed rate for a fixed period has reached a plateau.

14. The use of an inorganic oxygen-containing compound of a metal selected from the group consisting of metals capable of forming vanadates having a melting point within the range of from 650°C to 2000°C with vanadium of ash deposits from vanadium-containing fuel which inorganic oxygen-containing compound when heated up in a combustion flame liberates a gaseous substance by evaporation to form the corresponding oxide having a crystalline, porous low density structure, or the corresponding oxide obtained by heating the inorganic oxygen-containing compound at a temperature which is high enough to give the oxide in crystalline porous low density but is below the melting point of the oxide, said inorganic oxygen-containing compound and said crystalline porous low density oxide having a particle size distribution essentially within the range of from 0.1 to 2 micron, preferably from 0.1 to 1 microns, as a component of fuel additive compositions for the reduction/removal of vanadium-containing ash deposits.

and dispersant coating under centrifugal or oscillation forces and/or to ultrasonic treatment to a particle size distribution as stated above.

5

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C10L 1/10, C10L 10/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3067018 A (V. VOORHEES), 4 December 1962 (04.12.62), column 1, line 71 - column 2, line 3; column 2, line 10 - line 12; column 4, line 27 - line 53, column 8, line 51 - line 65, claim 9	1-14
X	US 3205053 A (ANDREW T. MCCORD), 7 Sept 1965 (07.09.65), column 2, line 49 - line 60, claim 1	1-14
A	US 5637118 A (NORMAN S. BORNSTEIN ET AL), 10 June 1997 (10.06.97), column 2, line 54 - line 60, claim 1, abstract	1-14

[X] Further documents are listed in the continuation of Box C.   [X] See patent family annex.

* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 December 2003	1 6 -12- 2003

Name and mailing address of the ISA/	Authorized officer
Swedish Patent Office Box 5055, S-102 42 STOCKHOLM	Mårten Hulthén/ELY
Facsimile No. + 46 8 666 02 86	Telephone No. + 46 8 782 25 00

Form PCT/ISA/210 (second sheet) (July 1998)

C (Continuation).   DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1459032 A (UNITED AIRCRAFT CORPORATION), 22 December 1976 (22.12.76), claim 1	1-14
A	GB 689579 A (HERBERT THOMAS SHIRLEY), 1 April 1953 (01.04.53), page 2, line 114 - page 3, line 11	1-14
A	US 2781005 A (T.A. TAYLOR ET AL), 12 February 1957 (12.02.57), column 2, line 3 - line 8; column 4, line 13 - line 15	1-14
A	GB 2216138 A (DIETROL LIMITED), 4 October 1989 (04.10.89), page 2, line 10 - line 12, claim 1	1-14
A	US 3692503 A (IRA KUKIN), 19 Sept 1972 (19.09.72), column 7, line 23 - line 36	1-14
A	DATABASE WPI Week 198228 Derwent Publications Ltd., London, GB; AN 1982-58050E & JP 57089485 A (NALCO CHEM CO), 3 June 1982 (1982-06-03)	1-14
A	US 4412844 A (JOHN H. COLLINS ET AL), 1 November 1983 (01.11.83), claim 1	1-14

INTERNATIONAL SEARCH REPORT
Information on patent family members

31/10/03

Patent document cited in search report			Publication date	Patent family member(s)			Publication date
US	3067018	A	04/12/62	NONE			
US	3205053	A	07/09/65	FR GB NL	1325217 1005957 278128	A A A	26/04/63 29/09/65 00/00/00
US	5637118	A	10/06/97	US	RE36117	E	02/03/99
GB	1459032	A	22/12/76	AU DE FR IT JP	6847174 2421927 2229861 1012237 50014911	A A A B A	06/11/75 05/12/74 13/12/74 10/03/77 17/02/75
GB	689579	A	01/04/53	NONE			
US	2781005	A	12/02/57	CH FR GB	306059 1045851 731242	A A A	31/03/55 01/12/53 08/06/55
GB	2216138	A	04/10/89	GB GB	8804874 8904499	D D	00/00/00 00/00/00
US	3692503	A	19/09/72	NONE			
US	4412844	A	01/11/83	CA	1128751	A	03/08/82

Form PCT/ISA/210 (patent family annex) (July 1998)